

# PATENT ABSTRACTS OF JAPAN

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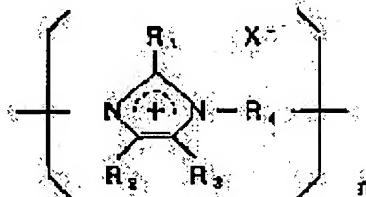
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## (54) CHARGE CONTROLLING AGENT AND ELECTROPHOTOGRAPHIC TONER

### (57)Abstract:

**PURPOSE:** To obtain a charge controlling agent and a toner excellent independency of charges and picture qualities against environmental conditions which is diffused to generate bad odorous matter by using a charge controlling agent comprising a specified polymer quaternary salt.

**CONSTITUTION:** A charge controlling agent comprising a polymer quaternary salt expressed by formula is used. In formula, R1 is a hydrogen atom or hydrocarbon group of 1-17 carbon number, R2 and R3 are independently hydrogen atoms or hydrocarbon groups of 1-8 carbon number, or R2 and R3 connect with each other to form an aromatic ring. R4 is an alkylene group of 1-12 carbon number which may contain an ether coupling, X- is an anion, and (n) is an integer 2-100. This charge controlling agent is incorporated into an electrophotographic toner containing at least a binder resin and coloring agent. In formula, R1 is preferably hydrogen or alkyl group of 11-17 carbon number, R2 and R3 are preferably hydrogen, methyl groups, ethyl groups and benzo groups, and R4 is preferably a trimethylene group, tetramethylene group, hexamethylene group, etc.



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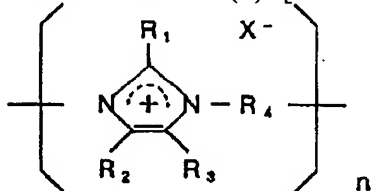
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## CLAIMS

[Claim(s)]

[Claim 1] The electric charge control agent characterized by consisting of the 4th class salt of a macromolecule shown by the following general formula (1).

General formula (1): [Formula 1]



(Among a formula, as for R1, R2 and R3 are hydrogen or the hydrocarbon group of C1 - C8 independently respectively about hydrogen or the hydrocarbon group of C1 - C17, or R2 and R3 are connected mutually and they may form the ring.) R4 About the alkylene group of C1 - C12 which may include ether linkage in the radical, it is X. - n expresses the integer of 2-100 for an anion.

[Claim 2] The toner for electrophotography characterized by containing an electric charge control agent according to claim 1 further in the toner for electrophotography which contains binder resin and a coloring agent at least:

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to an electric charge control agent and the toner for electrophotography. It is related with the electric charge control agent of forward electrification nature, and the toner for electrophotography using this in more detail.

[0002]

[Description of the Prior Art] The development by the xerography makes the toner charged by friction with a carrier, a sleeve, etc. adsorb electrostatic to the electrostatic latent image formed on the photo conductor, and is performed by carrying out heating fixing of the toner which imprinted this toner in the paper and imprinted it further with a hot calender roll or flash plate light. So, in order to obtain a clear image, it is necessary to adjust this toner so that it may have the proper amount of electrifications. The electric charge control agent of forward or negative electrification nature is added from the former by the toner for electrophotography in order to control this amount of electrifications. Among these, as an object of a macromolecule system, the block polymer (resin of USP4,925,764 publication etc.) of polyamine resin (resin given in JP,53-13284,B etc.), the acrylic resin (resin given in JP,62-210472,A etc.) which has a quarternary-ammonium-salt radical, a quarternary-ammonium-salt radical content polymer, and an oleophilic polymer etc. is known for the electric charge control agent of forward electrification nature.

[0003] On the other hand, reducing the malodorous substance generated from electrophotography equipments, such as a copying machine, is proposed from the problem of the environmental side of office in recent years. The component in a toner for which the low volatile matter in a toner volatilizes with heating when a toner being established pyrolyzes that a malodorous substance is generated from electrophotography equipment, and it is mainly based on the cause of low volatile matter occurring. Reducing the residual styrene monomer in toner binder resin, impurity aldehydes (JP,3-101746,A etc.), etc. is proposed in order to reduce this malodorous substance. However, when their eyes were turned to the electric charge control agent which is the constituent of the toner on a par with a toner binder, each object of a macromolecule system was lacking in thermal resistance at the electric charge control agent of the forward electrification nature known conventionally, and when it used for a copying machine etc. as a toner, it decomposed, and there was a problem of generating unpleasant amine-like odour. As what solves this problem, the heat-resistant high 4th class salt (JP,62-264066,A publication) of a macromolecule is proposed.

[0004]

[Problem(s) to be Solved by the Invention] However, when the 4th class salt of said macromolecule is used as an electric charge control agent, there is a problem that an image with it is not obtained. [ the large environmental dependency of the amount of electrifications of a toner and ] [ clear on the day of rainy weather ]

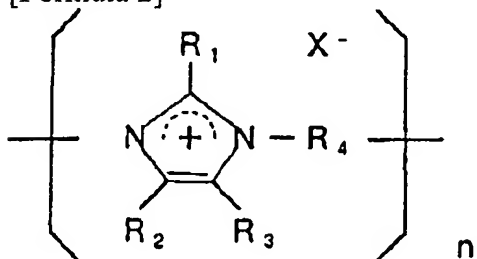
[0005]

[Means for Solving the Problem] this invention persons reached this invention, as a result of inquiring

wholeheartedly for the purpose of obtaining the electric charge control agent and toner which were hard to generate a malodorous substance and were excellent in the amount of electrifications, and the environmental dependency of copy image quality. Namely, the electric charge control agent characterized by this invention consisting of the 4th class salt of a giant molecule shown by the following general formula (1); it is the toner for electrophotography characterized by containing the above-mentioned electric charge control agent further in the toner for electrophotography which contains binder resin and a coloring agent at least in a list.

General formula (1) : [0006]

[Formula 2]



[0007] (Among a formula, as for R1, R2 and R3 are hydrogen or the hydrocarbon group of C1 - C8 independently respectively about hydrogen or the hydrocarbon group of C1 - C17, or R2 and R3 are connected mutually and they may form the ring.) R4 About the alkylene group of C1 - C12 which may include ether linkage in the radical, it is X. - n expresses the integer of 2-100 for an anion.

[0008] It sets to a general formula (1) and is R1. As hydrogen or a hydrocarbon group of C1 - C17 hydrogen and the alkyl group (a methyl group, an ethyl group, and n-propyl group --) of C1 - C17 An iso-propyl group, n-butyl, a cyclohexyl radical, n-pentyl radical, An undecyl radical, a tridecyl radical, a pentadecyl group, a heptadecyl radical, etc., An alkenyl radical (an undecenyl radical, a tridecenyl radical, heptadecenyl radical, etc.), Alkylphenyl radicals (a pentyl phenyl group, a hexyl phenyl group, an octyl phenyl group, a nonylphenyl radical, DESHIRU phenyl group, etc.), aryl groups (phenyl group etc.), aralkyl radicals (benzyl etc.), etc. are mentioned. Things desirable [ among these ] are hydrogen and the alkyl group of C11-C17, and still more desirable things are an undecyl radical, a tridecyl radical, a pentadecyl group, and a heptadecyl radical.

[0009] R2 And R3 Hydrogen, or C1 - C8 As a hydrocarbon group, hydrogen, alkyl groups (a methyl group, an ethyl group, a propyl group, butyl, a hexyl group, octyl radical, etc.), aryl groups (phenyl group etc.), aralkyl radicals (benzyl etc.), etc. are mentioned. R2 R3 A benzoradical etc. is mentioned as a ring connected mutually. Things desirable [ among these ] are hydrogen, a methyl group, an ethyl group, and a benzoradical, and still more desirable things are hydrogen and a benzoradical.

[0010] R4 As an alkylene group of C1 - C12, a methylene group, ethylene, a trimethylene radical, a tetramethylen radical, a hexamethylene radical, an octamethylene radical, a deca methylene group, a dodeca methylene group, etc. are mentioned inside. Moreover, R4 As an alkylene group of C1 which includes ether linkage inside - C12, -CH2CH2OCH2CH2-, -CH2CH2OCH2OCH2CH2-, -CH2CH2OCH2CH2OCH2CH2-, etc. are mentioned. Things desirable [ among these ] are ethylene, a trimethylene radical, a tetramethylen radical, a hexamethylene radical, -CH2CH2OCH2CH2-, and -CH2CH2OCH2OCH2CH2-, and still more desirable things are a trimethylene radical, a tetramethylen radical, a hexamethylene radical, and -CH2CH2OCH2CH2-.

[0011] as the anion of X- halogen ion (a chlorine ion and bromine ion --) sulfate ion, such as iodine ion, nitrate ion, perchlorate ion, and sulfonic-acid ion (p-toluenesulfonic-acid ion --) Methylsulfonic acid ion, hydroxy naphth sulfonic-acid ion, etc., carboxylic-acid ion (formic acid ion, acetic-acid ion, and propionic-acid ion --) Boric-acid ion (boric-acid ion, metaboric acid ion, tetrafluoroboric acid ion, tetraphenyl borate ion, etc.), such as benzoic-acid ion, metal oxo acid ion (molybdic-acid ion, tungstic-acid ion, etc.), etc. are mentioned. Things desirable [ among these ] are carboxylic-acid ion, sulfonic-acid ion, boric-acid ion, and oxo acid ion.

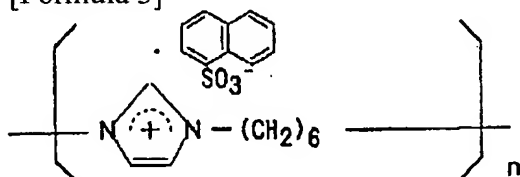
[0012] The number average degree of polymerizations n of the 4th class salt of this macromolecule are

2-100, and are usually 4-30 preferably [ it is desirable and ] to 3-50, and a pan.

[0013] Instantiation of the example of the electric charge control agent of this invention mentions the compound respectively shown by the following-izing 3 --izing 11.

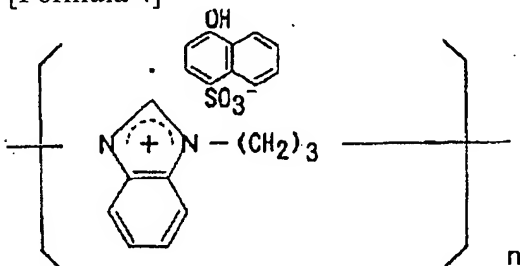
[0014]

[Formula 3]



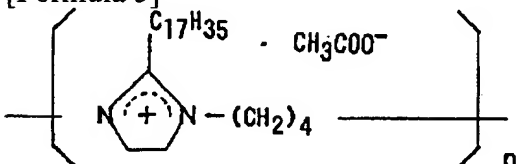
[0015]

[Formula 4]



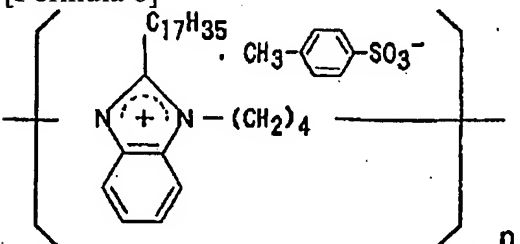
[0016]

[Formula 5]



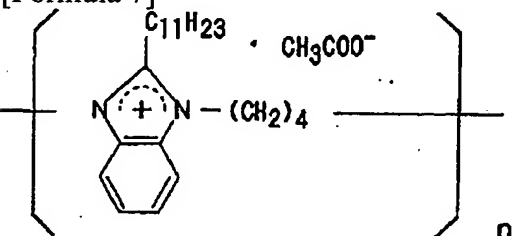
[0017]

[Formula 6]



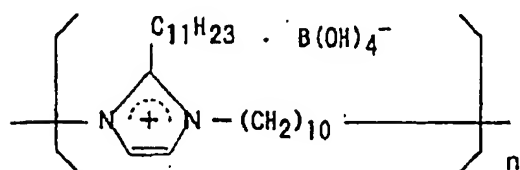
[0018]

[Formula 7]



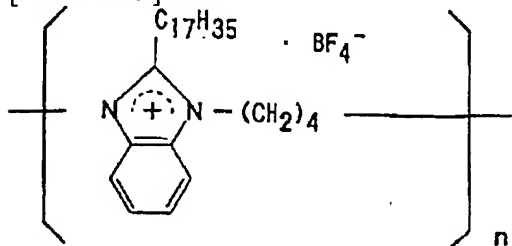
[0019]

[Formula 8]



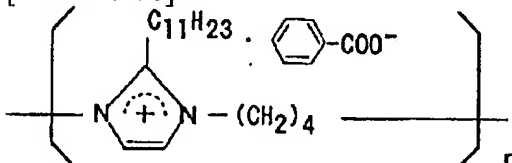
[0020]

[Formula 9]



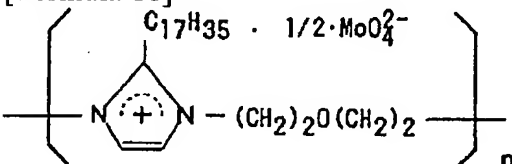
[0021]

[Formula 10]



[0022]

[Formula 11]



[0023] When the manufacture approach of the electric charge control agent of this invention is illustrated, there is an approach to which imidazole derivatives (A) and dihalide (B) are made to react. As imidazole derivatives (A) -- an imidazole and an alkyl imidazole (2-methylimidazole --) 2-ethyl imidazole, 2-propyl imidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2, 4-dimethyl imidazole, 4, 5-dimethyl imidazole, etc., Aryl imidazoles (2-phenylimidazole etc.), benzimidazole, alkyl benzimidazole (2-methyl benzimidazole and 2-ethylbenzo imidazole --) Arylbenzo imidazoles (2-phenylbenzo imidazole etc.), such as 2-propyl benzimidazole, 2-undecyl benzimidazole, and 2-heptadecyl benzimidazole, etc. are mentioned. As dihalide (B), alkylene dihalide, aralkylene (ethylene dichloride, ethylene dibromide, 1,3-dibromopropane, 1, 4-dichlorobutane, 1,4-dibromobutane, 1, 6-dibromo hexane, 1, 8-dibromo octane, 1, 10-dibromo decane, 1, 12-dibromo dodecane, etc.) dihalide (xylylene dichloride etc.), the alkylene dihalide (- dichloroethyl ether, and beta and beta'beta, beta'-dichloro ethyl formal etc.) that includes ether linkage in a radical are mentioned. the reaction ratio of imidazole derivatives (A) and dihalide (B) -- mol criteria -- it is -- usually -- 1:2 to 1.5:1 -- it is -- desirable -- 1:1.3 to 1.3:1 -- it is 1:1.2 to 1.2:1 still more preferably. Moreover, mono-halide or N permutation imidazole can be used together in order to block the polymerization object end of the 4th class salt of a macromolecule if needed. As mono-halide, a methyl chloride, a methyl iodide, an ethyl bromide, a n-butyl bromide, a butyl chloride, a benzyl chloride, a benzyl bromide, etc. are mentioned. As an N permutation imidazole, 1-methyl imidazole, 1-ethyl imidazole, 1-benzyl imidazole, 1-methyl benzimidazole, 1-ethylbenzo imidazole, 1-benzyl benzimidazole, etc. are mentioned. X - The alkali metal and ammonium salt of an anion other than a halogen can also be used together in order to make an

anion into anions other than the halogen illustrated above.

[0024] As a reaction solvent, what is necessary is just inactive to (A) and (B). For example, alcohols solvents, such as aprotic polar solvents, such as ketones, such as aromatic series solvents, such as benzene, toluene, and a xylene, an acetone, and a methyl ethyl ketone, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide, a methanol, ethanol, and isopropanol, water, and these partially aromatic solvents are mentioned. They are an alcohols solvent and an aprotic solvent preferably [ among these ]. It is desirable to use alkali together in order to neutralize the hydrogen halide generated by the reaction. As alkali, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, etc. are mentioned. Although it is desirable that dihalide (B) is dropped into imidazole derivatives (A) and the solution of alkali as for the reaction approach, it can also teach coincidence. After removing the mineral salt which sub<sup>\*\*</sup>(ed) according to filtration or centrifugal separation after reaction termination, a solvent is distilled out, and the electric charge control agent of this invention is obtained. When a water-soluble solvent like a methanol, ethanol, and dimethylformamide is used for a reaction solvent, by pouring a reaction mixture underwater, mineral salt and a solvent can be removed to coincidence, and the 4th class salt of a macromolecule of powder-like this invention can also be obtained. Reaction temperature is usually 30-200 degrees C, and is 60-180 degrees C preferably. Since it will be easy to start side reaction at less than 30 degrees C if a reaction rate is slow and 200 degrees C is exceeded, it is not desirable. Although reaction time changes also with reaction temperature, it is usually about 2 - 20 hours.

[0025] As BAIMBA resin which can be used for the toner for electrophotography of this invention, although styrene resin, polyolefine system resin, polyester system resin, epoxy system resin, polyurethane system resin, these mixed resin, etc. are mentioned, if it is binder resin which can be used for toners, it is good and anything is not limited especially.

[0026] As styrene resin, the homopolymer of styrene and the copolymer of styrene and the monomer in which other copolymerization is possible are mentioned. As styrene and a monomer which can be copolymerized, aromatic series vinyl hydrocarbons other than styrene, an acrylic (meta) monomer, and other monomers are mentioned. As an aromatic series vinyl hydrocarbon, the substitution product (alpha methyl styrene, p-methyl styrene, p-cumyl styrene, etc.) of styrene, for example, alkylation styrene, halogenation styrene (KURORU styrene, KURORU methyl styrene, etc.), acetoxystyrene, hydroxystyrene, etc. are mentioned. (Meta) As an acrylic monomer, acrylate (meta) {the alkyl (meta) acrylate [methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, lauryl (meta) acrylate, stearyl (meta) acrylate], etc. of C1 - C18, hydroxyl content (meta) acrylate (hydroxyethyl (meta) acrylate etc.), etc.} and a nitrile group content monomer [(meta) acrylonitrile] etc. are mentioned. Moreover, as other monomers, vinyl ester, aliphatic series vinyl (vinyl acetate, propionic-acid vinyl, etc.) hydrocarbons (a butadiene, isoprene, etc.), halogenation olefins (a vinyl chloride, vinyl bromide, etc.), partial saturation monochrome or polycarboxylic acid [(meta) an acrylic acid, ethacrylic acid, a crotonic acid, a sorbic acid, a maleic acid, an itaconic acid, a cinnamic acid], etc., those anhydrides, those partial ester (maleic anhydride etc.) (maleic-acid monomethyl ester etc.), etc. are mentioned. Desirable things are the polymerization object of styrene, the copolymerization object of styrene and an acrylic (meta) monomer, the copolymerization object of styrene and an aliphatic series vinyl hydrocarbon, and the copolymerization object of the monomer in which these and other little copolymerization are possible among styrene resin.

[0027] As polyolefine system resin, the following (b) - (d)s, and two or more sorts of such mixture are mentioned, for example.

(\*\*): Polyethylene, polypropylene, an ethylene alpha olefin (carbon numbers 3-8) copolymer (for example, ethylene 50wt% more than, especially 70wt(s)% more than thing)

(\*\*): maleic-acid derivative (maleic-anhydride, maleic-acid dimethyl ester, maleic-acid diethyl ester, maleic-acid G 2-ethylhexyl ester, etc.) addition product (Ha): of I -- oxide (\*\*) of (\*\*) -- : -- the copolymer of ethylene nature unsaturated carboxylic acid [(meta) an acrylic acid, an itaconic acid], etc., and/or the ester [alkyl (C1-C18) ester] etc. and ethylene nature unsaturated hydrocarbon (ethylene, a propylene, butene-1, etc.) -- desirable things are polyethylene, polypropylene, and these maleic-acid derivatives among these.



[0028] As polyester system resin, the polycondensation object of dicarboxylic acid components, such as dicarboxylic acid and/or its ester plasticity derivative (low-grade alkyl ester, acid halide, acid anhydride), and a diol component etc. is mentioned. As a dicarboxylic acid component, aliphatic series dicarboxylic acid, such as aliphatic series dicarboxylic acid of the carbon numbers 2-30, such as aromatic series dicarboxylic acid, such as a terephthalic acid, isophthalic acid, a phthalic acid, naphthalene dicarboxylic acid, trimellitic acid and those ester (dimethyl terephthalate etc.), and acid halide (terephthalic-acid dichloride etc.), an adipic acid, a sebacic acid, and dodecane dibasic acid, and those ester (adipic-acid dimethyl etc.), and acid halide (AJIPI acid dichloride etc.), is mentioned. It is concomitant use of aromatic series dicarboxylic acid and aromatic series dicarboxylic acid, and aliphatic series dicarboxylic acid preferably [ among these ]. As a diol component, ethylene glycol, 1,3-propanediol, Aliphatic series diols, such as aliphatic series diols, such as 1,4-butanediol, 1,6-hexanediol, and neopentyl glycol, and alcoholates (the sodium alcoholate etc.) of those Bisphenol A, Bisphenol S, Bisphenol F, hydroquinone, Aromatic series diols, such as those ester (diacetyl bisphenol A etc.) and those alcoholates (bisphenol A disodium alcoholate etc.) The ethyleneoxide and/or the propylene oxide addition product of bisphenol A, Aromatic series diol alkylene oxide addition products, such as ethyleneoxide of Bisphenol F, and/or a propylene oxide addition product Polyalkylene glycols, such as a polyethylene glycol, a polypropylene glycol, and a polytetramethylene glycol, are mentioned. Things desirable [ among these ] are aromatic series diol alkylene oxide addition products, aliphatic series diols, and those concomitant use, and still more desirable things are aromatic series diol alkylene oxide addition products.

[0029] As epoxy system resin, an addition condensation object, its denaturation object, etc. of bisphenol A and epichlorohydrin are mentioned.

[0030] As polyurethane system resin, the polyaddition object of a diisocyanate component and a diol component etc. is mentioned. As a diisocyanate component, aliphatic series diisocyanate, such as cycloaliphatic diisocyanate, such as aromatic series diisocyanate, such as TDI and MDI, isophorone diisocyanate, and Hydrogenation MDI, and ethylene di-isocyanate, and tetramethylene di-isocyanate, etc. is mentioned. It is aromatic series diisocyanate preferably [ among these ]. The object used for polyester as a diol component and the same object are mentioned. It is an aromatic series diol alkylene oxide addition product preferably [ it is / among these / desirable and ] to an aromatic series diol alkylene oxide addition product, aliphatic series diols and those concomitant use, and a pan.

[0031] As a coloring agent, the pigment and color which are usually used for toners can be used. Carbon black, iron black, etc. as a black coloring agent for example, as a red coloring agent Lysol red, Watchung Red, and carmine 6B, the lake red C As a yellow [ red / CROMOPHTAL ] coloring agent, although Cu-phthalocyanine etc. is mentioned as a blue coloring agent and a chloro-ized Cu-phthalocyanine etc. is mentioned as a green stain agent, benzidine yellow, Hansa yellow, the CROMOPHTAL yellow, etc. It is not limited to these that there should just be high tinting strength.

[0032] As occasion demands, the toner for electrophotography of this invention can also contain magnetic powder (compounds, such as powder of ferromagnetic metals, such as iron, cobalt, and nickel, or magnetite, hematite, and a ferrite).

[0033] Based on the weight of a toner, magnetic powder the rate of each constituent in the toner for electrophotography of this invention 0.5 to 10% 30 to 99% 0.1 to 10% usually It consists of what was used 0 to 50%. [ the electric charge control agent of this invention ] [ binder resin ] [ a coloring agent ] Furthermore, other electric charge control agent] (Nigrosine, quarternary ammonium salt, etc.) can be included if needed [ various additive [lubricant (polytetrafluoroethylene, low-molecular-weight polyolefine, a fatty acid its metal salt, or amide) and if needed / various ] as occasion demands. The amount of these additives is usually 0 - 5% based on toner weight.

[0034] After the toner for electrophotography carries out the dry type blend of the above-mentioned component based on a well-known technique, melting kneading is carried out, and coarse grinding of it is carried out after that, and, finally it is atomized using a jet pulverizer etc. Furthermore it is classified and particle size is usual. It is obtained as a particle which is 5-20 microns. It is mixed with carrier particles, such as iron powder, a glass bead, nickel powder, and a ferrite, if needed, and said toner for

electrophotography is used as a developer of an electric latent image. Moreover, hydrophobic colloidal silica impalpable powder etc. can also be used for fluid amelioration of a toner.

[0035]

[Example] Although an example explains this invention further below, thereby, this invention is not limited. Each section expresses the weight section among an example.

[0036] The [synthetic example 1] imidazole 190 section, the carbonic anhydride soda 148 section and 1, and 6-dibromo hexane 681 section was reacted under reflux at 80 degrees C in the DMF1000 section for 8 hours for 1 hour. After cooling, the 1-naphthalene sulfonic-acid soda 642 section and the water 1000 section were added, and it stirred for 1 hour. The mineral salt which sub\*\*(ed) was carried out the \*\* exception after distilling out water, DMF was distilled out further, and the electric charge control agent (1) of this invention was obtained.

[0037] The [synthetic example 2] benzimidazole 298 section, the carbonic anhydride soda 134 section, and the 1,3-dibromopropane 458 section were reacted under reflux at 80 degrees C in the DMF1000 section for 4 hours for 1 hour. Subsequently, the benzyl chloride 64 section was added and it reacted under reflux for 4 hours. After cooling, the 4-hydroxy naphthalene sulfonic-acid soda 622 section and the water 1000 section were added, and it stirred for 1 hour. The mineral salt which sub\*\*(ed) was carried out the \*\* exception after distilling out water, DMF was distilled out further, and the electric charge control agent (2) of this invention was obtained.

[0038] The [synthetic example 3] heptadecyl imidazole 694 section, the carbonic anhydride soda 120 section, and the 1,4-dibromobutane 407 section were reacted under reflux at 80 degrees C in the DMF1000 section for 4 hours for 1 hour. Subsequently, the benzyl chloride 96 section was added and it reacted under reflux for 4 hours. Said reaction mixture was added into the water solution which dissolved the sodium acetate 186 section in the water 2000 section, and it stirred violently for 1 hour. The polymer which deposited was dried the back according to \*\*, and the electric charge control agent (3) of this invention was obtained.

[0039] The [synthetic example 4] heptadecyl benzimidazole 599 section, the carbonic anhydride soda 89 section, and the 1,4-dibromobutane 327 section were reacted under reflux at 80 degrees C in the DMF1000 section for 4 hours for 1 hour. Subsequently, the benzyl chloride 43 section was added and it reacted under reflux for 4 hours. Said reaction mixture was added into the water solution which dissolved the Para toluenesulfonic acid soda 326 section in the water 2000 section, and it stirred violently for 1 hour. The polymer which deposited was dried the back according to \*\*, and the electric charge control agent (4) of this invention was obtained.

[0040] The [synthetic example 5] undecyl benzimidazole 682 section, the carbonic anhydride soda 133 section, and the 1,4-dibromobutane 487 section were reacted under reflux at 80 degrees C in the DMF1000 section for 4 hours for 1 hour. Subsequently, the benzyl chloride 63 section was added and it reacted under reflux for 4 hours. Said reaction mixture was added into the water solution which dissolved the sodium acetate 206 section in the water 2000 section, and it stirred violently for 1 hour. The polymer which deposited was dried the back according to \*\*, and the electric charge control agent (5) of this invention was obtained.

[0041] The [synthetic example 6] undecyl imidazole 497 section, the carbonic anhydride soda 118 section and 1, and the 10-dibromo decane 559 section were reacted under reflux at 80 degrees C in the DMF1000 section for 4 hours for 1 hour. Subsequently, the benzyl chloride 94 section was added and it reacted under reflux for 4 hours. Said reaction mixture was added into the water solution which dissolved the metaphoric acid soda 228 section in the water 2000 section, and it stirred violently for 1 hour. The polymer which deposited was dried the back according to \*\*, and the electric charge control agent (6) of this invention was obtained.

[0042] The [synthetic example 7] heptadecyl benzimidazole 697 section, the carbonic anhydride soda 104 section, and the 1,4-dibromobutane 380 section were reacted under reflux at 80 degrees C in the DMF1000 section for 4 hours for 1 hour. Subsequently, the benzyl chloride 50 section was added and it reacted under reflux for 4 hours. Said reaction mixture was added into the water solution which dissolved the HOUFUTSU-ized sodium 215 section in the water 2000 section, and it stirred violently for

1 hour. The polymer which deposited was dried the back according to \*\*, and the electric charge control agent (7) of this invention was obtained.

[0043] The [synthetic example 8] undecyl imidazole 530 section, the carbonic anhydride soda 126 section, and the 1,4-dibromobutane 429 section were reacted under reflux at 80 degrees C in the DMF1000 section for 4 hours for 1 hour. Subsequently, the benzyl chloride 101 section was added and it reacted under reflux for 4 hours. Said reaction mixture was added into the mixture of the benzoic-acid soda 343 section and the water 2000 section, and it stirred violently for 1 hour. The polymer which deposited was dried the back according to \*\*, and the electric charge control agent (8) of this invention was obtained.

[0044] The [synthetic example 9] heptadecyl imidazole 654 section, the carbonic anhydride soda 113 section, and the 2-chloro ethyl ether 275 section were reacted under reflux at 80 degrees C in the DMF1000 section for 4 hours for 1 hour. Subsequently, the benzyl chloride 54 section was added and it reacted under reflux for 4 hours. Said reaction mixture was added into the water solution which dissolved the sodium molybdate 258 section in the water 2000 section, and it stirred violently for 1 hour. The polymer which deposited was dried the back according to \*\*, and the electric charge control agent (9) of this invention was obtained.

[0045] The epichlorohydrin 408 section was dropped at the mixture of the [example 1 of comparison composition] undecyl imidazole 97.9 section, and the water 600 section at 50 degrees C in 2 hours. Subsequently, it reacted at 100 degrees C for 16 hours, and after cooling, the 4-hydroxy naphthalene sulfonic-acid soda 1085 section was added, and it stirred for 1 hour. The polymer which deposited was carried out the \*\* exception and the comparison electric charge control agent (1) was obtained.

[0046] The polymerization of the mixed monomer of the [example 2 of comparison composition] styrene 570 section and the 4th class salt 30 of methyl chloride section of dimethylaminoethyl methacrylate was carried out at 65 degrees C by making the azobis dimethylvaleronitrile 10 section into an initiator for 10 hours in a methanol / toluene (3/1) partially aromatic solvent 400 section. Reduced pressure drying ground with the jet mill after distilling out a solvent, and the comparison electric charge control agent (2) was obtained.

[0047] [Examples 1-9 and the examples 1-2 of a comparison]

According to the presentation ratio of the [creation of toner] following table 1, it pulverized after preliminary mixing with the Henschel mixer, and an electric charge control agent, binder resin, the coloring agent, and the release agent were pulverized with the jet mill after kneading and coarse grinding with the biaxial extruder, and, subsequently carried out pneumatic elutriation, and toner [ of this invention with a volume mean particle diameter of about 11 micrometers ] (1) - (9) and a comparison toner (1), and (2) were obtained. The ferrite carrier 96 section with a particle size of 100-150 micrometers which carried out the coat of toner (1) - (9) and a comparison toner (1), and the (2) 4 section and the silicon resin of this invention was mixed, and it considered as 2 component developer. The copy test of the above-mentioned developer was performed using the electrophotography copying machine which attached the OPC photo conductor of [copy test] marketing. The developer was sampled in part out of the copying machine to coincidence, and the amount of electrifications was measured by the blowing off method. Moreover, it measured also about the odor generated from the exhaust port of a copying machine. The result is shown in the following table 2.

[0048]

[Table 1]

No	荷電制御剤	バインダー樹脂	着色剤	離型剤
実施例 1	制御剤 (1) 3部	ハイ- GRX2500*1 100部	リ-カ' A330R*2 4部	ビ' スコ- A550P*3 2部
実施例 2	制御剤 (2) 3部	ハイ- GRX2500*1 100部	リ-カ' A330R*2 4部	ビ' スコ- A550P*3 2部
実施例 3	制御剤 (3) 2部	ハイ- GRX2500*1 100部	リ-カ' A330R*2 5部	ビ' スコ- A550P*3 2部
実施例 4	制御剤 (4) 2部	ハイ- GRX2500*1 100部	リ-カ' A330R*2 6部	ビ' スコ- A550P*3 2部
実施例 5	制御剤 (5) 2部	ハイ- GRX2500*1 100部	リ-カ' A330R*2 6部	ビ' スコ- A660P*4 2部
実施例 6	制御剤 (6) 2部	ハイ- TB9000*5 100部	リ-カ' A330R*2 6部	ビ' スコ- A660P*4 2部
実施例 7	制御剤 (7) 3部	ハイ- TB9000*5 100部	リ-カ' A330R*2 6部	ビ' スコ- A660P*4 2部
実施例 8	制御剤 (8) 4部	ハイ- EX-1*6 100部	リ-カ' A330R*2 4部	-----
実施例 9	制御剤 (9) 3部	ビ' スコ- 1009*7 100部	#4920*8 3部	ビ' スコ- A550P*3 2部
比較例 1	比較 (1) 3部	ハイ- GRX2500*1 100部	リ-カ' A330R*2 6部	ビ' スコ- A550P*3 2部
比較例 2	比較 (2) 10部	ハイ- TB9000*5 100部	リ-カ' A330R*2 8部	ビ' スコ- A660P*4 2部
*1	スチレン/アクリル樹脂	三洋化成工業製		
*2	カーボンブラック	キャボット社製		
*3	低分子量PP-WAX	三洋化成工業製		
*4	低分子量PP-WAX	三洋化成工業製		
*5	スチレン/アクリル樹脂	三洋化成工業製		
*6	ポリエステル樹脂	三洋化成工業製		
*7	エポキシ樹脂	シェル社製		
*8	Cu-フタロシアニン	大日精化製		

[0049]

[Table 2]

No	帯電量 ( $\mu\text{C/g}$ )		複写面質				複写時の 臭気
	中温中湿*1	高温高湿*2	中温	中湿*1	高温	高湿*2	
実施例 1	+ 6. 5	+ 6. 2	○		○		臭気なし
実施例 2	+ 7. 3	+ 7. 1	○		○		臭気なし
実施例 3	+ 1 2. 4	+ 1 1. 9	◎		◎		臭気なし
実施例 4	+ 1 0. 3	+ 8. 8	◎		◎		臭気なし
実施例 5	+ 1 1. 8	+ 1 1. 4	◎		○		臭気なし
実施例 6	+ 1 3. 1	+ 1 2. 8	◎		◎		臭気なし
実施例 7	+ 8. 5	+ 8. 6	◎		◎		臭気なし
実施例 8	+ 7. 4	+ 6. 8	○		△		臭気なし
実施例 9	+ 1 0. 2	+ 8. 7	◎		○		臭気なし
比較例 1	+ 9. 5	+ 6. 8	○	×	かぶり		臭気なし
比較例 2	+ 8. 5	+ 8. 1	◎		○		アミン臭発生
複写面質 : ◎ 非常に良い ○ 良い △ やや悪い × 悪い							
測定温湿度: *1: 20℃、50%RH *2: 30℃、80%RH							

[0050]

[Effect of the Invention] The electric charge control agent and the toner for electrophotography of this invention have the following descriptions.

\*\* Excel in thermal resistance, and when it uses for a copying machine etc., don't generate unpleasant amine-like odour.

\*\* It excels in the environmental stability of the amount of electrifications, and the amount of electrifications and copy image quality cannot be easily influenced of the weather.

\*\* There is little coloring of an electric charge control agent, and when it is used for color toners other than black, such as red, blue, and yellow, the toner of skillful coloring is made.

[Translation done.]

## \* NOTICES \*

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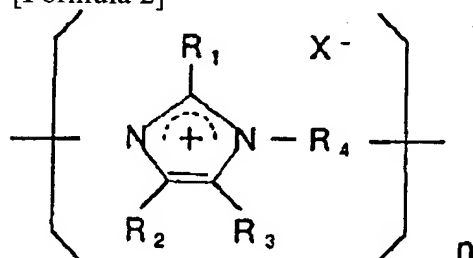
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## MEANS

[Means for Solving the Problem] this invention persons reached this invention, as a result of inquiring wholeheartedly for the purpose of obtaining the electric charge control agent and toner which were hard to generate a malodorous substance and were excellent in the amount of electrifications, and the environmental dependency of copy image quality. Namely, the electric charge control agent characterized by this invention consisting of the 4th class salt of a giant molecule shown by the following general formula (1); it is the toner for electrophotography characterized by containing the above-mentioned electric charge control agent further in the toner for electrophotography which contains binder resin and a coloring agent at least in a list.

General formula (1) : [0006]

[Formula 2]



[0007] (Among a formula, as for R1, R2 and R3 are hydrogen or the hydrocarbon group of C1 - C8 independently respectively about hydrogen or the hydrocarbon group of C1 - C17, or R2 and R3 are connected mutually and they may form the ring.) R4 About the alkylene group of C1 - C12 which may include ether linkage in the radical, it is X. - n expresses the integer of 2-100 for an anion.

[0008] It sets to a general formula (1) and is R1. As hydrogen or a hydrocarbon group of C1 - C17 hydrogen and the alkyl group (a methyl group, an ethyl group, and n-propyl group --) of C1 - C17 An iso-propyl group, n-butyl, a cyclohexyl radical, n-pentyl radical, An undecyl radical, a tridecyl radical, a pentadecyl group, a heptadecyl radical, etc., An alkenyl radical (an undecenyl radical, a tridecenyl radical, heptadecenyl radical, etc.), Alkylphenyl radicals (a pentyl phenyl group, a hexyl phenyl group, an octyl phenyl group, a nonylphenyl radical, DESHIRU phenyl group, etc.), aryl groups (phenyl group etc.), aralkyl radicals (benzyl etc.), etc. are mentioned. Things desirable [ among these ] are hydrogen and the alkyl group of C11-C17, and still more desirable things are an undecyl radical, a tridecyl radical, a pentadecyl group, and a heptadecyl radical.

[0009] R2 And R3 Hydrogen, or C1 - C8 As a hydrocarbon group, hydrogen, alkyl groups (a methyl group, an ethyl group, a propyl group, butyl, a hexyl group, octyl radical, etc.), aryl groups (phenyl group etc.), aralkyl radicals (benzyl etc.), etc. are mentioned. R2 R3 A benzoradical etc. is mentioned as a ring connected mutually. Things desirable [ among these ] are hydrogen, a methyl group, an ethyl group, and a benzoradical, and still more desirable things are hydrogen and a benzoradical.

[0010] R4 As an alkylene group of C1 - C12, a methylene group, ethylene, a trimethylene radical, a tetramethylen radical, a hexamethylene radical, an octamethylene radical, a deca methylene group, a

dodeca methylene group, etc. are mentioned inside. Moreover, R4 As an alkylene group of C1 which includes ether linkage inside - C12, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-, etc. are mentioned. Things desirable [ among these ] are ethylene, a trimethylene radical, a tetramethylen radical, a hexamethylene radical, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-, and -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-, and still more desirable things are a trimethylene radical, a tetramethylen radical, a hexamethylene radical, and -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-.

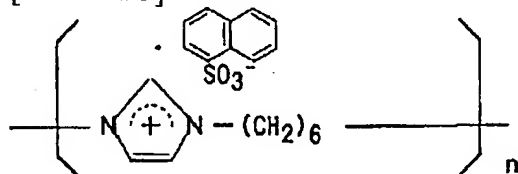
[0011] as the anion of X- halogen ion (a chlorine ion and bromine ion --) sulfate ion, such as iodine ion, nitrate ion, phosphoric-acid ion, and sulfonic-acid ion (p-toluenesulfonic-acid ion --) Methylsulfonic acid ion, hydroxy naphth sulfonic-acid ion, etc., carboxylic-acid ion (formic acid ion, acetic-acid ion, and propionic-acid ion --) Boric-acid ion (boric-acid ion, metaboric acid ion, tetrafluoroboric acid ion, tetraphenyl borate ion, etc.), such as benzoic-acid ion, metal oxo acid ion (molybdic-acid ion, tungstic-acid ion, etc.), etc. are mentioned. Things desirable [ among these ] are carboxylic-acid ion, sulfonic-acid ion, boric-acid ion, and oxo acid ion.

[0012] The number average degree of polymerizations n of the 4th class salt of this macromolecule are 2-100, and are usually 4-30 preferably [ it is desirable and ] to 3-50, and a pan.

[0013] Instantiation of the example of the electric charge control agent of this invention mentions the compound respectively shown by the following-izing 3 --izing 11.

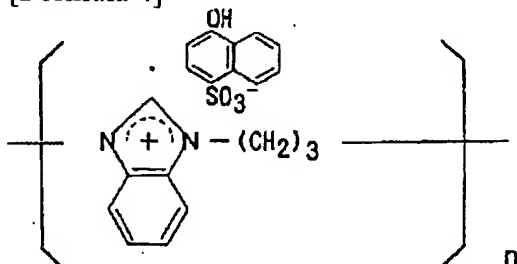
[0014]

[Formula 3]



[0015]

[Formula 4]

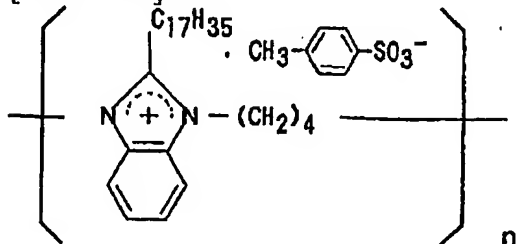


[0016]

[Formula 5]

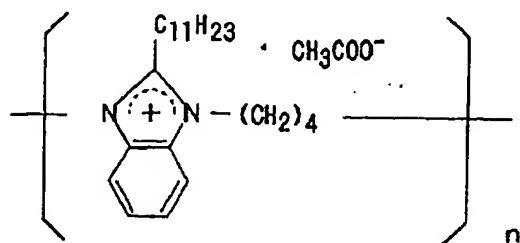
[0017]

[Formula 6]



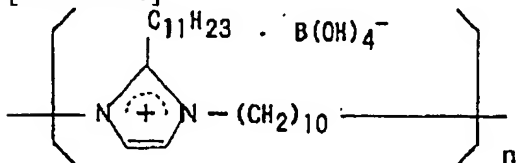
[0018]

[Formula 7]



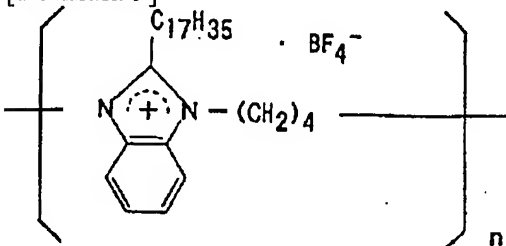
[0019]

[Formula 8]



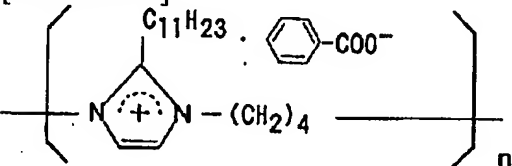
[0020]

[Formula 9]



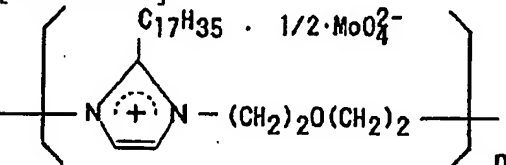
[0021]

[Formula 10]



[0022]

[Formula 11]



[0023] When the manufacture approach of the electric charge control agent of this invention is illustrated, there is an approach to which imidazole derivatives (A) and dihalide (B) are made to react. as imidazole derivatives (A) -- an imidazole and an alkyl imidazole (2-methylimidazole --) 2-ethyl imidazole, 2-propyl imidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2, 4-dimethyl imidazole, 4, 5-dimethyl imidazole, etc., Aryl imidazoles (2-phenylimidazole etc.), benzimidazole, alkyl benzimidazole (2-methyl benzimidazole and 2-ethylbenzo imidazole --) Arylbenzo imidazoles (2-phenylbenzo imidazole etc.), such as 2-propyl benzimidazole, 2-undecyl benzimidazole, and 2-heptadecyl benzimidazole, etc. are mentioned. As dihalide (B), alkylene dihalide, aralkylene (ethylene dichloride, ethylene dibromide, 1,3-dibromopropane, 1, 4-dichlorobutane, 1,4-dibromobutane, 1, 6-dibromo hexane, 1, 8-dibromo octane, 1, 10-dibromo decane, 1, 12-dibromo dodecane, etc.) dihalide (xylylene dichloride etc.), the alkylene dihalide (- dichloroethyl ether, and beta and beta'beta, beta'-



dichloro ethyl formal etc.) that includes ether linkage in a radical are mentioned. the reaction ratio of imidazole derivatives (A) and dihalide (B) -- mol criteria -- it is -- usually -- 1:2 to 1.5:1 -- it is -- desirable -- 1:1.3 to 1.3:1 -- it is 1:1.2 to 1.2:1 still more preferably. Moreover, mono-halide or N permutation imidazole can be used together in order to block the polymerization object end of the 4th class salt of a macromolecule if needed. As mono-halide, a methyl chloride, a methyl iodide, an ethyl bromide, a n-butyl bromide, a butyl chloride, a benzyl chloride, a benzyl bromide, etc. are mentioned. As an N permutation imidazole, 1-methyl imidazole, 1-ethyl imidazole, 1-benzyl imidazole, 1-methyl benzimidazole, 1-ethylbenzo imidazole, 1-benzyl benzimidazole, etc. are mentioned. X - The alkali metal and ammonium salt of an anion other than a halogen can also be used together in order to make an anion into anions other than the halogen illustrated above.

[0024] As a reaction solvent, what is necessary is just inactive to (A) and (B). For example, alcohols solvents, such as aprotic polar solvents, such as ketones, such as aromatic series solvents, such as benzene, toluene, and a xylene, an acetone, and a methyl ethyl ketone, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide, a methanol, ethanol, and isopropanol, water, and these partially aromatic solvents are mentioned. They are an alcohols solvent and an aprotic solvent preferably [ among these ]. It is desirable to use alkali together in order to neutralize the hydrogen halide generated by the reaction. As alkali, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, etc. are mentioned. Although it is desirable that dihalide (B) is dropped into imidazole derivatives (A) and the solution of alkali as for the reaction approach, it can also teach coincidence. After removing the mineral salt which sub\*\* (ed) according to filtration or centrifugal separation after reaction termination, a solvent is distilled out, and the electric charge control agent of this invention is obtained. When a water-soluble solvent like a methanol, ethanol, and dimethylformamide is used for a reaction solvent, by pouring a reaction mixture underwater, mineral salt and a solvent can be removed to coincidence, and the 4th class salt of a macromolecule of powder-like this invention can also be obtained. Reaction temperature is usually 30-200 degrees C, and is 60-180 degrees C preferably. Since it will be easy to start side reaction at less than 30 degrees C if a reaction rate is slow and 200 degrees C is exceeded, it is not desirable. Although reaction time changes also with reaction temperature, it is usually about 2 - 20 hours.

[0025] As BAIMBA resin which can be used for the toner for electrophotography of this invention, although styrene resin, polyolefine system resin, polyester system resin, epoxy system resin, polyurethane system resin, these mixed resin, etc. are mentioned, if it is binder resin which can be used for toners, it is good and anything is not limited especially.

[0026] As styrene resin, the homopolymer of styrene and the copolymer of styrene and the monomer in which other copolymerization is possible are mentioned. As styrene and a monomer which can be copolymerized, aromatic series vinyl hydrocarbons other than styrene, an acrylic (meta) monomer, and other monomers are mentioned. As an aromatic series vinyl hydrocarbon, the substitution product (alpha methyl styrene, p-methyl styrene, p-cumyl styrene, etc.) of styrene, for example, alkylation styrene, halogenation styrene (KURORU styrene, KURORU methyl styrene, etc.), acetoxy styrene, hydroxystyrene, etc. are mentioned. (Meta) As an acrylic monomer, acrylate (meta) {the alkyl (meta) acrylate [methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, lauryl (meta) acrylate, stearyl (meta) acrylate], etc. of C1 - C18, hydroxyl content (meta) acrylate (hydroxyethyl (meta) acrylate etc.), etc.} and a nitrile group content monomer [(meta) acrylonitrile] etc. are mentioned. Moreover, as other monomers, vinyl ester, aliphatic series vinyl (vinyl acetate, propionic-acid vinyl, etc.) hydrocarbons (a butadiene, isoprene, etc.), halogenation olefins (a vinyl chloride, vinyl bromide, etc.), partial saturation monochrome or polycarboxylic acid [(meta) an acrylic acid, ethacrylic acid, a crotonic acid, a sorbic acid, a maleic acid, an itaconic acid, a cinnamic acid], etc., those anhydrides, those partial ester (maleic anhydride etc.) (maleic-acid monomethyl ester etc.), etc. are mentioned. Desirable things are the polymerization object of styrene, the copolymerization object of styrene and an acrylic (meta) monomer, the copolymerization object of styrene and an aliphatic series vinyl hydrocarbon, and the copolymerization object of the monomer in which these and other little copolymerization are possible among styrene resin.

[0027] As polyolefine system resin, the following (b) - (d)s, and two or more sorts of such mixture are

mentioned, for example.

(\*\*): Polyethylene, polypropylene, an ethylene alpha olefin (carbon numbers 3-8) copolymer (for example, ethylene 50wt% more than, especially 70wt(s)% more than thing)

(\*\*): maleic-acid derivative (maleic-anhydride, maleic-acid dimethyl ester, maleic-acid diethyl ester, maleic-acid G 2-ethylhexyl ester, etc.) addition product (Ha): of I -- oxide (\*\*) of (\*\*) -- : -- the copolymer of ethylene nature unsaturated carboxylic acid [(meta) an acrylic acid, an itaconic acid], etc., and/or the ester [alkyl (C1-C18) ester] etc. and ethylene nature unsaturated hydrocarbon (ethylene, a propylene, butene-1, etc.) -- desirable things are polyethylene, polypropylene, and these maleic-acid derivatives among these.

[0028] As polyester system resin, the polycondensation object of dicarboxylic acid components, such as dicarboxylic acid and/or its ester plasticity derivative (low-grade alkyl ester, acid halide, acid anhydride), and a diol component etc. is mentioned. As a dicarboxylic acid component, aliphatic series dicarboxylic acid, such as aliphatic series dicarboxylic acid of the carbon numbers 2-30, such as aromatic series dicarboxylic acid, such as a terephthalic acid, isophthalic acid, a phthalic acid, naphthalene dicarboxylic acid, trimellitic acid and those ester (dimethyl terephthalate etc.), and acid halide (terephthalic-acid dichloride etc.), an adipic acid, a sebacic acid, and dodecane dibasic acid, and those ester (adipic-acid dimethyl etc.), and acid halide (AJIPI acid dichloride etc.), is mentioned. It is concomitant use of aromatic series dicarboxylic acid and aromatic series dicarboxylic acid, and aliphatic series dicarboxylic acid preferably [ among these ]. As a diol component, ethylene glycol, 1,3-propanediol, Aliphatic series diols, such as aliphatic series diols, such as 1,4-butanediol, 1,6-hexanediol, and neopentyl glycol, and alcoholates (the sodium alcoholate etc.) of those Bisphenol A, Bisphenol S, Bisphenol F, hydroquinone, Aromatic series diols, such as those ester (diacetyl bisphenol A etc.) and those alcoholates (bisphenol A disodium alcoholate etc.) The ethyleneoxide and/or the propylene oxide addition product of bisphenol A, Aromatic series diol alkylene oxide addition products, such as ethyleneoxide of Bisphenol F, and/or a propylene oxide addition product Polyalkylene glycols, such as a polyethylene glycol, a polypropylene glycol, and a polytetramethylene glycol, are mentioned. Things desirable [ among these ] are aromatic series diol alkylene oxide addition products, aliphatic series diols, and those concomitant use, and still more desirable things are aromatic series diol alkylene oxide addition products.

[0029] As epoxy system resin, an addition condensation object, its denaturation object, etc. of bisphenol A and epichlorohydrin are mentioned.

[0030] As polyurethane system resin, the polyaddition object of a diisocyanate component and a diol component etc. is mentioned. As a diisocyanate component, aliphatic series diisocyanate, such as cycloaliphatic diisocyanate, such as aromatic series diisocyanate, such as TDI and MDI, isophorone diisocyanate, and Hydrogenation MDI, and ethylene di-isocyanate, and tetramethylene di-isocyanate, etc. is mentioned. It is aromatic series diisocyanate preferably [ among these ]. The object used for polyester as a diol component and the same object are mentioned. It is an aromatic series diol alkylene oxide addition product preferably [ it is / among these / desirable and ] to an aromatic series diol alkylene oxide addition product, aliphatic series diols and those concomitant use, and a pan.

[0031] As a coloring agent, the pigment and color which are usually used for toners can be used. Carbon black, iron black, etc. as a black coloring agent for example, as a red coloring agent Lysol red, Watchung Red, and carmine 6B, the lake red C As a yellow [ red / CROMOPHTAL ] coloring agent, although Cu-phthalocyanine etc. is mentioned as a blue coloring agent and a chloro-ized Cu-phthalocyanine etc. is mentioned as a green stain agent, benzidine yellow, Hansa yellow, the CROMOPHTAL yellow, etc. It is not limited to these that there should just be high tinting strength.

[0032] As occasion demands, the toner for electrophotography of this invention can also contain magnetic powder (compounds, such as powder of ferromagnetic metals, such as iron, cobalt, and nickel, or magnetite, hematite, and a ferrite).

[0033] Based on the weight of a toner, magnetic powder the rate of each constituent in the toner for electrophotography of this invention 0.5 to 10% 30 to 99% 0.1 to 10% usually It consists of what was used 0 to 50%. [ the electric charge control agent of this invention ] [ binder resin ] [ a coloring agent ]

Furthermore, other electric charge control agent] (Nigrosine, quaternary ammonium salt, etc.) can be included if needed [ various additive [lubricant (polytetrafluoroethylene, low-molecular-weight polyolefine, a fatty acid its metal salt, or amide) and if needed / various ] as occasion demands. The amount of these additives is usually 0 - 5% based on toner weight.

[0034] After the toner for electrophotography carries out the dry type blend of the above-mentioned component based on a well-known technique, melting kneading is carried out, and coarse grinding of it is carried out after that, and, finally it is atomized using a jet pulverizer etc. Furthermore it is classified and particle size is usual. It is obtained as a particle which is 5-20 microns. It is mixed with carrier particles, such as iron powder, a glass bead, nickel powder, and a ferrite, if needed, and said toner for electrophotography is used as a developer of an electric latent image. Moreover, hydrophobic colloidal silica impalpable powder etc. can also be used for fluid amelioration of a toner.

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[Translation done.]

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(54)【発明の名称】 荷電制御剤および電子写真用トナー

(57)【要約】

【目的】加熱により悪臭を発生することなく、また帯電量の環境依存性が少ない電子写真用トナーを得ること。

【構成】イミダゾリウム塩骨格を持つ高分子4級塩からなる荷電制御剤を含有する電子写真用トナーである。

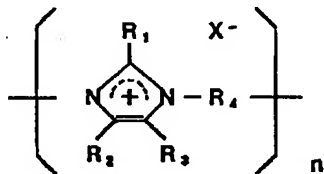
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## 【特許請求の範囲】

【請求項1】下記一般式(1)で示される高分子4級塩からなることを特徴とする荷電制御剤。

一般式(1)：

【化1】



(式中、R<sub>1</sub> は水素またはC<sub>1</sub>～C<sub>17</sub>の炭化水素基を、R<sub>2</sub> およびR<sub>3</sub> は各々独立に、水素またはC<sub>1</sub>～C<sub>8</sub>の炭化水素基であるか、あるいはR<sub>2</sub> とR<sub>3</sub> は相互に連結されて芳香環を形成していてもよい。R<sub>4</sub> は基中にエーテル結合を含んでいても良いC<sub>1</sub>～C<sub>12</sub>のアルキレン基を、X<sup>-</sup> はアニオンを、nは2～100の整数を表す。)

【請求項2】少なくともバインダー樹脂および着色剤を含有する電子写真用トナーにおいて、更に請求項1記載の荷電制御剤を含有することを特徴とする電子写真用トナー。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は荷電制御剤および電子写真用トナーに関する。さらに詳しくは正帯電性の荷電制御剤およびこれを用いた電子写真用トナーに関する。

【0002】

【従来の技術】電子写真法による現像は、感光体上に形成された静電潜像に対し、キャリアやスリーブ等との摩擦によって帯電されたトナーを静電的に吸着させ、このトナーを紙上に転写し、さらに転写したトナーを熱ロールもしくはフラッシュ光等にて加熱定着することにより行われる。それゆえ、このトナーは鮮明な画像を得るために、適正な帯電量を有するように調整する必要がある。この帯電量を制御する目的で、従来から電子写真用トナーには正または負帯電性の荷電制御剤が添加されている。このうち、正帯電性の荷電制御剤で高分子系の物としては、ポリアミン樹脂(特公昭53-13284号公報記載の樹脂など)、4級アンモニウム塩基を有するアクリル系樹脂(特開昭62-210472号公報記載の樹脂など)、4級アンモニウム塩基含有ポリマーと親油性ポリマーのブロックポリマー(USP4, 925, 764記載の樹脂など)などが知られている。

【0003】一方、近年オフィスの環境面の問題から、複写機等の電子写真装置から発生する悪臭物質を低減することが提案されている。電子写真装置から悪臭物質が発生するのは、主にトナーを定着する時の加熱によってトナー中の低揮発分が揮発する、トナー中の成分が熱分解し低揮発分が発生する等の原因によるものである。この悪臭物質を低減する目的で、トナーバインダー樹脂中

2

の残存スチレンモノマー、不純物アルデヒド(特開平3-101746号公報など)などを低減することが提案されている。しかしながらトナーバインダーと並ぶトナーの構成成分である荷電制御剤に目を向けると、従来知られている正帯電性の荷電制御剤で高分子系の物はいずれも耐熱性に乏しく、トナーとして複写機等に用いた時に分解し、不快なアミン臭を発生するという問題があった。この問題を解決するものとして、耐熱性の高い高分子4級塩(特開昭62-264066号公報記載)が提案されている。

【0004】

【発明が解決しようとする課題】しかしながら、前記高分子4級塩を荷電制御剤として用いた場合は、トナーの帯電量の環境依存性が大きく雨天の日には鮮明な画像が得られないという問題がある。

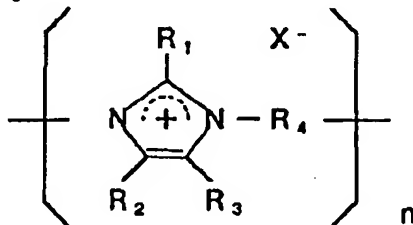
【0005】

【課題を解決するための手段】本発明者らは、悪臭物質が発生しにくく、かつ、帯電量、複写画質の環境依存性に優れた荷電制御剤およびトナーを得ることを目的に鋭意検討を行った結果、本発明に到達した。すなわち本発明は、下記一般式(1)で示される高分子4級塩からなることを特徴とする荷電制御剤；並びに、少なくともバインダー樹脂および着色剤を含有する電子写真用トナーにおいて、更に上記荷電制御剤を含有することを特徴とする電子写真用トナーである。

一般式(1)：

【0006】

【化2】



【0007】(式中、R<sub>1</sub> は水素またはC<sub>1</sub>～C<sub>17</sub>の炭化水素基を、R<sub>2</sub> およびR<sub>3</sub> は各々独立に、水素またはC<sub>1</sub>～C<sub>8</sub>の炭化水素基であるか、あるいはR<sub>2</sub> とR<sub>3</sub> は相互に連結されて芳香環を形成していてもよい。R<sub>4</sub> は基中にエーテル結合を含んでいても良いC<sub>1</sub>～C<sub>12</sub>のアルキレン基を、X<sup>-</sup> はアニオンを、nは2～100の整数を表す。)

【0008】一般式(1)において、R<sub>1</sub> の水素またはC<sub>1</sub>～C<sub>17</sub>の炭化水素基としては、水素、C<sub>1</sub>～C<sub>17</sub>のアルキル基(メチル基、エチル基、n-プロピル基、iso-プロピル基、n-ブチル基、シクロヘキシル基、n-ペンチル基、ウンデシル基、トリデシル基、ペンタデシル基、ヘプタデシル基など)、アルケニル基(ウンデセニル基、トリデセニル基、ヘプタデセニル基など)、アルキルフェニル基(ペンチルフェニル基、ヘキシルフェニル基、

3

オクチルフェニル基、ノニルフェニル基、デシルフェニル基など)、アリール基(フェニル基など)、アラルキル基(ベンジル基など)などが挙げられる。これらのうち好ましいものは、水素およびC<sub>11</sub>~C<sub>17</sub>のアルキル基であり、さらに好ましいものは、ウンデシル基、トリデシル基、ペンタデシル基、ヘプタデシル基である。

【0009】R<sub>2</sub> およびR<sub>3</sub> の水素またはC<sub>1</sub>~C<sub>8</sub> の炭化水素基としては、水素、アルキル基(メチル基、エチル基、プロピル基、ブチル基、ヘキシル基、オクチル基など)、アリール基(フェニル基など)およびアラルキル基(ベンジル基など)などが挙げられる。R<sub>2</sub> とR<sub>3</sub> が相互に連結された芳香環としてはベンゾ基などが挙げられる。これらのうち好ましいものは、水素、メチル基、エチル基およびベンゾ基であり、さらに好ましいものは水素およびベンゾ基である。

【0010】R<sub>4</sub> のうち、C<sub>1</sub>~C<sub>12</sub>のアルキレン基としてはメチレン基、エチレン基、トリメチレン基、テトラメチレン基、ヘキサメチレン基、オクタメチレン基、デカメチレン基およびドデカメチレン基などが挙げられる。またR<sub>4</sub> のうちエーテル結合を含むC<sub>1</sub>~C<sub>12</sub>のアルキレン基としては、-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-、-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-、-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-などが挙げられる。これらのうち好ましいものはエチレン基、トリメチレン基、テトラメチレン基、ヘキサメチレン基、-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-、および-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-であり、さらに好ましいものはトリメチレン基、テトラメチレン基、ヘキサメチレン基および、-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-である。

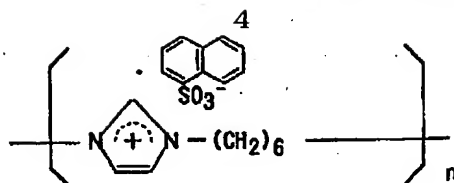
【0011】X<sup>-</sup> のアニオンとしてはハロゲンイオン(塩素イオン、臭素イオン、ヨウ素イオンなど)、硫酸イオン、硝酸イオン、リン酸イオン、スルホン酸イオン(ポトルエンスルホン酸イオン、メチルスルホン酸イオン、ヒドロキシナフトスルホン酸イオンなど)、カルボン酸イオン(蟻酸イオン、酢酸イオン、プロピオン酸イオン、安息香酸イオンなど)、ホウ酸イオン(ホウ酸イオン、メタホウ酸イオン、テトラフルオロホウ酸イオン、テトラフェニルホウ酸イオンなど)および金属オキソ酸イオン(モリブデン酸イオン、タングステン酸イオンなど)などが挙げられる。これらのうち好ましいものはカルボン酸イオン、スルホン酸イオン、ホウ酸イオンおよびオキソ酸イオンである。

【0012】該高分子4級塩の数平均重合度nは通常、2~100であり、好ましくは3~50、さらに好ましくは4~30である。

【0013】本発明の荷電制御剤の具体例を例示すると、下記化3~化11で各々示される化合物などが挙げられる。

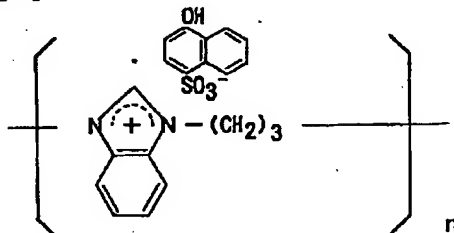
【0014】

【化3】



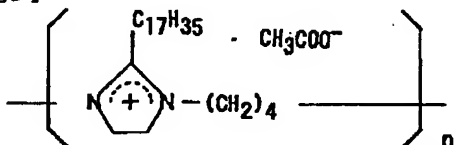
【0015】

【化4】



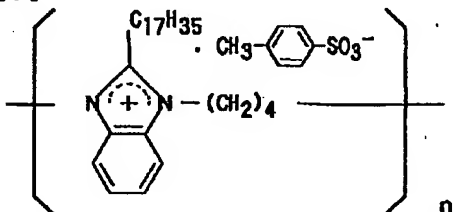
【0016】

【化5】



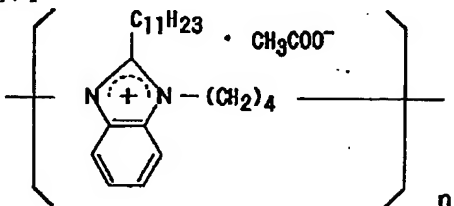
【0017】

【化6】



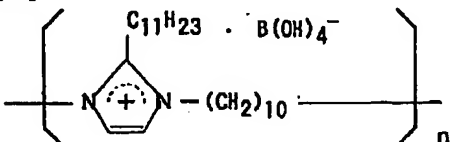
【0018】

【化7】



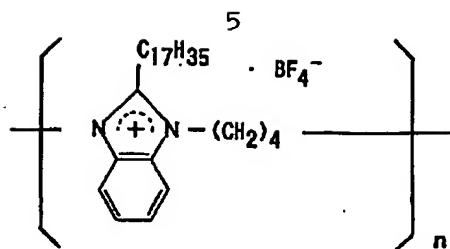
【0019】

【化8】



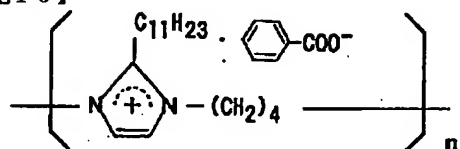
【0020】

【化9】



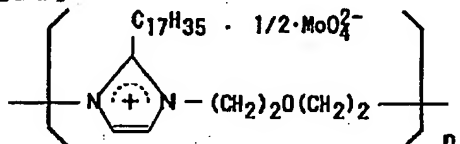
【0021】

【化10】



【0022】

【化11】



【0023】本発明の荷電制御剤の製造方法を例示すると、イミダゾール類(A)とジハライド(B)を反応せしめる方法等がある。イミダゾール類(A)としては、イミダゾール、アルキルイミダゾール(2-メチルイミダゾール、2-エチルイミダゾール、2-プロピルイミダゾール、2-ウンデシルイミダゾール、2-ヘプタデシルイミダゾール、2,4-ジメチルイミダゾール、4,5-ジメチルイミダゾールなど)、アリールイミダゾール(2-フェニルイミダゾールなど)、ベンゾイミダゾール、アルキルベンゾイミダゾール(2-メチルベンゾイミダゾール、2-エチルベンゾイミダゾール、2-プロピルベンゾイミダゾール、2-ウンデシルベンゾイミダゾール、2-ヘプタデシルベンゾイミダゾールなど)、アリールベンゾイミダゾール(2-フェニルベンゾイミダゾールなど)などが挙げられる。ジハライド(B)としてはアルキレンジハライド(エチレンジクロライド、エチレンジブロマイド、1,3-ジプロモプロパン、1,4-ジクロロブタン、1,4-ジプロモブタン、1,6-ジプロモヘキサン、1,8-ジプロモオクタン、1,10-ジプロモデカン、1,12-ジプロモドデカンなど)、アラルキレンジハライド(キシリレンジクロライドなど)、およびエーテル結合を基中に含むアルキレンジハライド( $\beta, \beta'$ -ジクロロエチルエーテル、 $\beta, \beta'$ -ジクロロエチルホルマルなど)などが挙げられる。イミダゾール類(A)とジハライド(B)の反応比はモル基準で、通常1:2~1.5:1であり、好ましくは1:1.3~1.3:1、さらに好ましくは1:1.2~1.2:1である。また、必要に応じて高分子4級塩の重合物末端を封鎖する目的でモノハライドまたはN置換イミダゾールを併用することができる。モノハライド

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としては塩化メチル、ヨウ化メチル、臭化エチル、臭化ブチル、塩化ブチル、塩化ベンジル、臭化ベンジルなどが挙げられる。N置換イミダゾールとしては1-メチルイミダゾール、1-エチルイミダゾール、1-ベンジルイミダゾール、1-メチルベンゾイミダゾール、1-エチルベンゾイミダゾール、1-ベンジルベンゾイミダゾールなどが挙げられる。X<sup>-</sup>のアニオンを前記に例示したハロゲン以外のアニオンにする目的でハロゲン以外のアニオンのアルカリ金属およびアンモニウム塩を併用することもできる。

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【0024】反応溶剤としては(A)および(B)に対し不活性なものであればよい。例えば、ベンゼン、トルエン、キシレン等の芳香族溶剤、アセトン、メチルエチルケトン等のケトン系溶剤、ジメチルホルムアミド、ジメチルアセトアミド、ジメチルスルホキシド等の非プロトン性極性溶剤、メタノール、エタノール、イソプロパノール等のアルコール系溶剤、水、およびこれらの混合溶剤が挙げられる。これらのうち好ましくはアルコール系溶剤および非プロトン性溶剤である。反応により発生するハロゲン化水素を中和する目的でアルカリを併用するのが好ましい。アルカリとしては水酸化ナトリウム、水酸化カリウムおよび炭酸ナトリウムなどが挙げられる。反応方法はイミダゾール類(A)およびアルカリの溶液中にジハライド(B)を滴下するのが好ましいが、同時に仕込むこともできる。反応終了後、副成した無機塩をろ過または遠心分離によりのぞいた後溶媒を溜去し、本発明の荷電制御剤が得られる。反応溶剤にメタノール、エタノール、ジメチルホルムアミドのような水溶性の溶媒を用いた場合は、反応混合物を水中に注ぐことにより無機塩および溶媒を同時に除去し、粉末状の本発明の高分子4級塩を得ることもできる。反応温度は通常30~200℃であり、好ましくは60~180℃である。30℃未満では反応速度が遅く、200℃を越えると副反応がおこりやすいので好ましくない。反応時間は反応温度によっても異なるが、通常2~20時間程度である。

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【0025】本発明の電子写真用トナーに使用し得るバインダー樹脂としては、スチレン系樹脂、ポリオレフィン系樹脂、ポリエステル系樹脂、エポキシ系樹脂、ポリウレタン系樹脂、これらの混合樹脂などが挙げられるが、トナー用に用いることができるバインダー樹脂なら何でもよく、特に限定されるものではない。

【0026】スチレン系樹脂としてはスチレンの単独重合体、およびスチレンと他の共重合可能な単量体の共重合体が挙げられる。スチレンと共重合可能な単量体としてはスチレン以外の芳香族ビニル炭化水素、(メタ)アクリル系単量体およびその他の単量体が挙げられる。芳香族ビニル炭化水素としてはスチレンの置換体たとえばアルキル置換スチレン( $\alpha$ -メチルスチレン、p-メチルスチレン、p-クロルスチレンなど)、ハロゲン置換

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スチレン(クロルスチレン、クロルメチルスチレンなど)、アセトキシスチレン、ヒドロキシスチレンなどが挙げられる。(メタ)アクリル系単量体としては(メタ)アクリレート〔C1～C18のアルキル(メタ)アクリレート〔メチル(メタ)アクリレート、エチル(メタ)アクリレート、ブチル(メタ)アクリレート、2-エチルヘキシル(メタ)アクリレート、ラウリル(メタ)アクリレート、ステアリル(メタ)アクリレートなど〕、ヒドロキシ基含有(メタ)アクリレート(ヒドロキシエチル(メタ)アクリレートなど)など〕およびニトリル基含有モノマー〔(メタ)アクリロニトリルなど〕が挙げられる。またその他の単量体としてはビニルエステル(酢酸ビニル、プロピオン酸ビニルなど)、脂肪族ビニル炭化水素(ブタジエン、イソプレンなど)、ハロゲン化オレフィン(塩化ビニル、臭化ビニルなど)、不飽和モノまたはポリカルボン酸〔(メタ)アクリル酸、エタアクリル酸、クロトン酸、ソルビン酸、マレイン酸、イタコン酸、ケイ皮酸など〕、それらの無水物(無水マレイン酸など)、それらの部分エステル(マレイン酸モノメチルエステルなど)などが挙げられる。スチレン系樹脂のうち好ましいものは、スチレンの重合体、スチレンと(メタ)アクリル系単量体の共重合体、スチレンと脂肪族ビニル炭化水素の共重合体およびこれらと少量の他の共重合可能な単量体の共重合体である。

【0027】ポリオレフィン系樹脂としては、例えば下記(イ)～(ニ)およびこれらの二種以上の混合物が挙げられる。

(イ)：ポリエチレン、ポリプロピレン、エチレン- $\alpha$ オレフィン(炭素数3～8)共重合体(例えばエチレン50wt%以上、とくに70wt%以上のもの)

(ロ)：(イ)のマレイン酸誘導体(無水マレイン酸、マレイン酸ジメチルエステル、マレイン酸ジエチルエステル、マレイン酸ジ-2-エチルヘキシルエステルなど)付加物

(ハ)：(イ)の酸化物

(ニ)：エチレン性不飽和カルボン酸〔(メタ)アクリル酸、イタコン酸など〕および/またはそのエステル〔アルキル(C1～C18)エステルなど〕とエチレン性不飽和炭化水素(エチレン、プロピレン、ブテン-1など)との共重合体これらのうち好ましいものはポリエチレン、ポリプロピレンおよびこれらのマレイン酸誘導体である。

【0028】ポリエステル系樹脂としてはジカルボン酸および/またはそのエステル形成性誘導体(低級アルキルエステル、酸ハライド、酸無水物)などのジカルボン酸成分とジオール成分との重縮合物などが挙げられる。ジカルボン酸成分としてはテレフタル酸、イソフタル酸、フタル酸、ナフタレンジカルボン酸、トリメリット酸およびそれらのエステル(テレフタル酸ジメチルなど)、酸ハライド(テレフタル酸ジクロライドなど)などの芳香族ジカルボン酸類、アジピン酸、セバシン酸、

ドデカン2塩基酸などの炭素数2～30の脂肪族ジカルボン酸およびそれらのエステル(アジピン酸ジメチルなど)、酸ハライド(アジピン酸ジクロライドなど)などの脂肪族ジカルボン酸類などが挙げられる。これらのうち好ましくは、芳香族ジカルボン酸類および芳香族ジカルボン酸類と脂肪族ジカルボン酸類の併用である。ジオール成分としてはエチレングリコール、1,3-アロパングジオール、1,4-ブタンジオール、1,6-ヘキサングジオール、ネオペンチルグリコールなどの脂肪族ジオールおよびそのアルコラート(そのナトリウムアルコラートなど)などの脂肪族ジオール類、ビスフェノールA、ビスフェノールS、ビスフェノールF、ヒドロキノン、それらのエステル(ジアセチルビスフェノールAなど)およびそれらのアルコラート(ビスフェノールAジナトリウムアルコラートなど)などの芳香族ジオール類、ビスフェノールAのエチレンオキシドおよび/またはプロピレンオキシド付加物、ビスフェノールFのエチレンオキシドおよび/またはプロピレンオキシド付加物などの芳香族ジオールアルキレンオキシド付加物類、ポリエチレングリコール、ポリプロピレングリコール、ポリテトラメチレングリコールなどのポリアルキレングリコール類などが挙げられる。これらのうち好ましいものは、芳香族ジオールアルキレンオキシド付加物類、脂肪族ジオール類、およびそれらの併用であり、さらに好ましいものは、芳香族ジオールアルキレンオキシド付加物類である。

【0029】エポキシ系樹脂としてはビスフェノールAとエピクロヒドリンの付加縮合物およびその変性物などが挙げられる。

【0030】ポリウレタン系樹脂としてはジイソシアネート成分とジオール成分の重付加物などが挙げられる。ジイソシアネート成分としてはTDI、MDIなどの芳香族ジイソシアネート、イソホロンジイソシアネート、水添MDIなどの脂環式ジイソシアネートおよびエチレンジイソシアネート、テトラメチレンジイソシアネートなどの脂肪族ジイソシアネートなどが挙げられる。これらのうち好ましくは芳香族ジイソシアネートである。ジオール成分としてはポリエステルに用いた物と同様な物が挙げられる。これらのうち好ましくは芳香族ジオールアルキレンオキシド付加物、脂肪族ジオール、およびそれらの併用、さらに好ましくは芳香族ジオールアルキレンオキシド付加物である。

【0031】着色剤としては、通常トナー用に使用されている顔料および染料を使うことができる。例えば、黒色着色剤としては、カーボンブラック、鉄黒等が、赤色着色剤としては、リゾールレッド、ウオッチングレッド、カーミン6B、レークレッドC、クロモフタールレッド等が、黄色着色剤としてはベンジジンイエロー、ハンザイエロー、クロモフタールイエロー等が、青色着色剤としてはCu-フタロシアニン等が、緑色着色剤とし



てはクロロ化Cu-フタロシアニン等が挙げられるが、高い着色力があればよく、これらに限定されるものではない。

【0032】本発明の電子写真用トナーは必要により、磁性粉（鉄、コバルト、ニッケルなどの強磁性金属の粉末もしくはマグネタイト、ヘマタイト、フェライトなどの化合物）を含有することもできる。

【0033】本発明の電子写真用トナー中の各構成成分の割合はトナーの重量に基づいて通常、本発明の荷電制御剤が0.1~10%、バインダー樹脂が30~99%、着色剤が0.5~10%、磁性粉が0~50%用いたものからなる。さらに必要により種々の添加剤〔滑剤（ポリテトラフルオロエチレン、低分子量ポリオレフィン、脂肪酸、もしくはその金属塩またはアミドなど）および必要に応じて他の荷電制御剤（ニグロシン、四級アンモニウム塩など）〕を含むことができる。これらの添加剤の量はトナー重量に基づいて通常0~5%である。

【0034】電子写真用トナーは公知の技術に基づき、上記の成分を乾式ブレンドした後、熔融混練され、その後粗粉砕され、最終的にジェット粉砕機などを用いて微粒化される。さらに分級されて粒径が通常5~20ミクロンの微粒として得られる。前記電子写真用トナーは必要に応じて鉄粉、ガラスビーズ、ニッケル粉、フェライトなどのキャリア粒子と混合されて電氣的潜像の現像剤として用いられる。またトナーの流動性改良のために疎水性コロイダルシリカ微粉末等を用いることもできる。

【0035】

【実施例】以下実施例により本発明をさらに説明するが、本発明はこれにより限定されるものではない。実施例中、部はいずれも重量部を表す。

【0036】〔合成例1〕イミダゾール190部、無水炭酸ソーダ148部および1,6-ジブプロモヘキサン681部をDMF1000部の中、80℃で1時間、還流下で8時間反応した。冷却後、1-ナフタレンスルホン酸ソーダ642部、および水1000部を加え1時間攪拌した。水を溜去後、副成した無機塩をろ別し、さらにDMFを溜去して、本発明の荷電制御剤（1）を得た。

【0037】〔合成例2〕ベンズイミダゾール298部、無水炭酸ソーダ134部および1,3-ジブプロモプロパン458部をDMF1000部の中、80℃で1時間、還流下で4時間反応した。次いでベンジルククロライド64部を加え、還流下で4時間反応した。冷却後、4-ヒドロキシナフタレンスルホン酸ソーダ622部、および水1000部を加え1時間攪拌した。水を溜去後、副成した無機塩をろ別し、さらにDMFを溜去して、本発明の荷電制御剤（2）を得た。

【0038】〔合成例3〕ヘプタデシルイミダゾール694部、無水炭酸ソーダ120部および1,4-ジブプロモタン407部をDMF1000部の中、80℃で1時間、還流下で4時間反応した。次いでベンジルククロライ

ド96部を加え、還流下で4時間反応した。酢酸ソーダ186部を水2000部に溶解した水溶液中に、前記反応混合物を加え、1時間激しく攪拌した。析出したポリマーをろ別後、乾燥し、本発明の荷電制御剤（3）を得た。

【0039】〔合成例4〕ヘプタデシルベンズイミダゾール599部、無水炭酸ソーダ89部および1,4-ジブプロモタン327部をDMF1000部の中、80℃で1時間、還流下で4時間反応した。次いでベンジルククロライド43部を加え、還流下で4時間反応した。パラトルエンスルホン酸ソーダ326部を水2000部に溶解した水溶液中に、前記反応混合物を加え、1時間激しく攪拌した。析出したポリマーをろ別後、乾燥し、本発明の荷電制御剤（4）を得た。

【0040】〔合成例5〕ウンデシルベンズイミダゾール682部、無水炭酸ソーダ133部および1,4-ジブプロモタン487部をDMF1000部の中、80℃で1時間、還流下で4時間反応した。次いでベンジルククロライド63部を加え、還流下で4時間反応した。酢酸ソーダ206部を水2000部に溶解した水溶液中に、前記反応混合物を加え、1時間激しく攪拌した。析出したポリマーをろ別後、乾燥し、本発明の荷電制御剤（5）を得た。

【0041】〔合成例6〕ウンデシルイミダゾール497部、無水炭酸ソーダ118部および1,10-ジブプロモカン559部をDMF1000部の中、80℃で1時間、還流下で4時間反応した。次いでベンジルククロライド94部を加え、還流下で4時間反応した。メタホウ酸ソーダ228部を水2000部に溶解した水溶液中に、前記反応混合物を加え、1時間激しく攪拌した。析出したポリマーをろ別後、乾燥し、本発明の荷電制御剤（6）を得た。

【0042】〔合成例7〕ヘプタデシルベンズイミダゾール697部、無水炭酸ソーダ104部および1,4-ジブプロモタン380部をDMF1000部の中、80℃で1時間、還流下で4時間反応した。次いでベンジルククロライド50部を加え、還流下で4時間反応した。ホウフッ化ナトリウム215部を水2000部に溶解した水溶液中に、前記反応混合物を加え、1時間激しく攪拌した。析出したポリマーをろ別後、乾燥し、本発明の荷電制御剤（7）を得た。

【0043】〔合成例8〕ウンデシルイミダゾール530部、無水炭酸ソーダ126部および1,4-ジブプロモタン429部をDMF1000部の中、80℃で1時間、還流下で4時間反応した。次いでベンジルククロライド101部を加え、還流下で4時間反応した。安息香酸ソーダ343部、水2000部の混合物中に、前記反応混合物を加え、1時間激しく攪拌した。析出したポリマーをろ別後、乾燥し、本発明の荷電制御剤（8）を得た。

【0044】〔合成例9〕ヘプタデシルイミダゾール6

54部、無水炭酸ソーダ113部および2-クロロエチルエーテル275部をDMF1000部の中、80℃で1時間、還流下で4時間反応した。次いでベンジクロライド54部を加え、還流下で4時間反応した。モリブデン酸ソーダ258部を水2000部に溶解した水溶液中に、前記反応混合物を加え、1時間激しく攪拌した。析出したポリマーをろ別後、乾燥し、本発明の荷電制御剤(9)を得た。

【0045】[比較合成例1] ウンデシルイミダゾール97.9部、水600部の混合物に50℃で、エピクロルヒドリン408部を2時間で滴下した。次いで、100℃で16時間反応し、冷却後、4-ヒドロキシナフタレンスルホン酸ソーダ1085部を加え1時間攪拌した。析出したポリマーをろ別し、比較荷電制御剤(1)を得た。

【0046】[比較合成例2] スチレン570部、ジメチルアミノエチルメタクリレートのメチルクロライド4級塩30部の混合モノマーをメタノール/トルエン(3/1)混合溶剤400部中で、アゾビスジメチルバレロニトリル10部を開始剤として、65℃で10時間重合

した。減圧乾燥により溶剤を溜去後、ジェットミルにて粉碎し、比較荷電制御剤(2)を得た。

【0047】[実施例1~9および比較例1~2]

【トナーの作成】下記表1の組成比に従って、荷電制御剤、バインダー樹脂、着色剤および離型剤をヘンシェルミキサで予備混合後、2軸押出機で混練、粗粉碎後、ジェットミルで微粉碎し、次いで風力分級し、体積平均粒径約11 $\mu$ mの本発明のトナー(1)~(9)および比較トナー(1)、(2)を得た。本発明のトナー(1)~(9)および比較トナー(1)、(2)4部とシリコン樹脂をコートした粒径100~150 $\mu$ mのフェライトキャリア96部を混合し2成分現像剤とした。

【複写テスト】市販のOPC感光体を付した電子写真複写機を用いて上記現像剤の複写テストをおこなった。同時に現像剤を複写機内から一部抜取り、帯電量をブローオフ法で測定した。また、複写機の排気口から発生する臭気についても測定した。その結果を下記表2に示す。

【0048】

【表1】

13		14		
No	荷電制御剤	バインダー樹脂	着色剤	離型剤
実施例1	制御剤(1) 3部	M17- GRX2500*1 100部	Y-3* M330R*2 4部	E* XJ-M550P*3 2部
実施例2	制御剤(2) 3部	M17- GRX2500*1 100部	Y-3* M330R*2 4部	E* XJ-M550P*3 2部
実施例3	制御剤(3) 2部	M17- GRX2500*1 100部	Y-3* M330R*2 5部	E* XJ-M550P*3 2部
実施例4	制御剤(4) 2部	M17- GRX2500*1 100部	Y-3* M330R*2 6部	E* XJ-M550P*3 2部
実施例5	制御剤(5) 2部	M17- GRX2500*1 100部	Y-3* M330R*2 6部	E* XJ-M660P*4 2部
実施例6	制御剤(6) 2部	M17- TB9000*5 100部	Y-3* M330R*2 6部	E* XJ-M660P*4 2部
実施例7	制御剤(7) 3部	M17- TB9000*5 100部	Y-3* M330R*2 6部	E* XJ-M660P*4 2部
実施例8	制御剤(8) 4部	M17- EX-1*6 100部	Y-3* M330R*2 4部	-----
実施例9	制御剤(9) 3部	E* XJ-T 1009*7 100部	#4920*8 3部	E* XJ-M550P*3 2部
比較例1	比較(1) 3部	M17- GRX2500*1 100部	Y-3* M330R*2 6部	E* XJ-M550P*3 2部
比較例2	比較(2) 10部	M17- TB9000*5 100部	Y-3* M330R*2 6部	E* XJ-M660P*4 2部
*1	スチレン/アクリル樹脂		三洋化成工業製	
*2	カーボンブラック		キャボット社製	
*3	低分子量PP-WAX		三洋化成工業製	
*4	低分子量PP-WAX		三洋化成工業製	
*5	スチレン/アクリル樹脂		三洋化成工業製	
*6	ポリエステル樹脂		三洋化成工業製	
*7	エポキシ樹脂		シェル社製	
*8	Cu-フタロシアニン		大日精化製	

15			16		
No	帯電量 (μC/g)		複写画質		複写時の臭気
	中温中湿*1	高温高湿*2	中温中湿*1	高温高湿*2	
実施例1	+6.5	+6.2	○	○	臭気なし
実施例2	+7.3	+7.1	○	○	臭気なし
実施例3	+12.4	+11.8	◎	◎	臭気なし
実施例4	+10.3	+8.9	◎	◎	臭気なし
実施例5	+11.8	+11.4	◎	○	臭気なし
実施例6	+13.1	+12.8	◎	◎	臭気なし
実施例7	+9.5	+9.6	◎	◎	臭気なし
実施例8	+7.4	+6.9	○	△	臭気なし
実施例9	+10.2	+9.7	◎	○	臭気なし
比較例1	+9.5	+6.8	○	× かぶり	臭気なし
比較例2	+8.5	+8.1	◎	○	アミン臭発生
複写画質 : ◎ 非常に良い    ○ 良い    △ やや悪い    × 悪い					
測定温湿度 : *1: 20℃、50%RH    *2: 30℃、80%RH					

## 【0050】

【発明の効果】本発明の荷電制御剤および電子写真用トナーは以下の特徴を有する。

①耐熱性に優れ、複写機等に用いた場合に不快なアミン臭を発生しない。

\* ②帯電量の環境安定性に優れ、帯電量および複写画質が天候の影響を受けにくい。

③荷電制御剤の着色が少なく、赤色、青色、黄色等の黒色以外のカラートナーに使用した場合、あざやかな発色のトナーができる。

\*